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## **ELECTROPLATING COMPOSITIONS AND METHODS FOR ELECTROPLATING**

### **Field**

5           This invention relates generally to electroplating compositions and methods for depositing conductive materials in features, such as trenches and/or contact holes formed on semiconductor workpieces.

### **Background**

10           In the production of semiconductor integrated circuits and other microelectronic articles from microelectronic workpieces, such as semiconductor wafers or semiconductor wafer substrates, it is often necessary to provide metal layers on a workpiece to serve as interconnect metallization that electrically connects various devices on the integrated circuit to one another.

15           Electrical interconnects have been conventionally formed in semiconductor devices by first depositing a conducting layer on a semiconductor workpiece (e.g., a wafer) surface using sputtering or similar techniques. Unnecessary portions of the conducting layer are removed through a chemical dry etch process with a pattern mask formed of photoresist or the like.

20           In earlier devices, aluminum or an aluminum alloy was used to form the wiring circuits. To keep up with the increased complexity of semiconductor devices, however, wiring in semiconductor devices has had to be made smaller and smaller. This in turn has lead to higher current densities and reduced lifetimes due to electromigration. In addition to this, shrinking lines result in higher resistance increasing RC  
25 (resistance/capacitance) delays.

          To avoid excessive RC delays and device failures due to electromigration, metals having superior conductivity and high electromigration resistance, such as copper, have been used to form the wiring. It is, however, difficult to perform dry etching on copper or a copper alloy that has been deposited over the entire workpiece

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surface (as in the process described above). Thus, a new approach known as damascene processing is used. For copper wires, first trenches or canals are formed according to a predetermined pattern in the workpiece surface for the wiring. In dual-damascene processing, contact holes or vias are also cut into the workpiece to connect one layer of metal to the overlying or underlying metal layer. Those trenches and/or contact holes are then filled with copper or a copper alloy. This method eliminates the process of removing unnecessary parts of the conductive layer by etching, requiring only that the surface of the workpiece be polished to remove the overburden of plated metal.

However the shapes of such wiring trenches and/or contact holes in today's device designs have a considerably high aspect ratio (the ratio of depth to width of the trenches and/or contact holes) as the width of the wiring gets smaller. The small dimensions (e.g., sub 1  $\mu\text{m}$  or even sub 0.25  $\mu\text{m}$ ) of device features, such as trenches and/or contact holes, make it difficult to fill the features with an even layer of metal using conventional sputtering methods for deposition of the metal. Chemical vapor deposition (CVD) has been used for depositing various materials, but it is difficult to prepare an appropriate gas material for copper or a copper alloy.

Electrolytic plating by immersing a workpiece into a plating solution has since been used to fill the trenches and/or contact holes with the necessary conductive material, typically copper or a copper alloy. Electroplating methods typically require a thin, continuous electrically conductive seed layer be deposited on the workpiece prior to the plating process. The seed layer generally is formed of a conductive metal, such as copper. Electroplating the desired metal is then generally accomplished by applying an electrical bias to the seed layer and exposing the workpiece, such as a wafer substrate, to an electroplating solution containing metal ions that will plate over the seed layer in the presence of the electrical bias.

An electroplating composition comprising copper (e.g., copper sulfate) and an acid or a conductive salt (e.g., sulfuric acid) may be used. The acid, such as sulfuric acid, is added to the electroplating composition to provide the high ionic conductivity to

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the plating composition necessary to achieve high throwing power. "Throwing power" refers to the ability of an electroplating composition to deposit metal uniformly on a workpiece, such as a wafer substrate. The acid does not participate in the electrode reactions, but provides conformal coverage of the plating material over the surface of the workpiece because acid reduces resistivity within the electroplating composition. If the composition has a low concentration of copper and a high concentration of acid, throwing power of the composition is improved.

A problem encountered with conventional plating solutions is that the deposition process within high aspect ratio trenches and/or contact holes is also influenced by mass transport, i.e., diffusion of the metal into the trenches and/or contact holes affects the kinetics of the deposition reaction in addition to the magnitude of the electric field (as is common on larger feature devices). Thus, the rate at which plating ions are provided to the surface of the workpiece can limit the plating rate, irrespective of the voltage or current density applied to the plating surface. Highly conductive electroplating compositions (e.g., high acid concentration compositions) that provide good throwing power do not obtain good coverage and fill within relatively small features on a device, i.e., sub-micron sized trenches and/or contact holes. This often causes a reduction in the quality of the deposit and leads to fill defects, typically voids. Voids are often formed when using such compositions for filling relatively small trenches and/or contact holes. In order to obtain good quality deposition, the deposition process must have high mass-transfer rates and low depletion of the reactant concentration near or within the small trenches and/or contact holes. However, in typical high acid plating baths the transport rates are limited by the relatively low metal ion concentration.

Transport of the metal ion to be plated is directly related to the concentration of the plated metal ion in the electroplating composition. A higher metal ion concentration results in a higher rate of transport of the metal into small features and in a higher metal ion concentration within the depletion layer, i.e., the boundary layer at the cathode surface hence, faster and better quality depositions may be achieved.

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When using a plating composition superior in throwing power and coating uniformity to fill copper in the trenches and/or contact holes of a substrate having relatively large aspect ratios, however, as mentioned above the filling capability of the composition is poor. The inlets of the trenches and/or contact holes are often blocked  
5 before the trenches and/or contact holes are filled, thereby tending to form voids. Voids may also be caused by other forces, such as non-uniform nucleation at the seed layer during a plating process, inadequate nucleation, and large grain formation during plating. Unfortunately, using a typical low acid, high metal plating composition provides inferior throwing power and suppressed additive activity, resulting in unplated  
10 areas within features.

A significant number of voids and/or non-uniform deposition typically result in a detrimentally lowered conductivity as well as poor electromigration resistance. In some cases, the void(s) and/or non-uniformity may be sufficiently large to cause an open circuit and the device fails.

15 Put simply, as known to those of ordinary skill in the relevant art, if the plating composition has a low concentration of copper and a high concentration of acid, the plating composition will have high conductivity and good polarization, thereby improving throwing power. In contrast, if the plating composition has a high concentration of copper and a low concentration of acid, it is known that the  
20 composition will have good transport of the metal ions. In other words, the concentration of metal ions will be sufficient at bottom of the high aspect ratio trenches and/or contact holes to allow good feature filling.

Attempts to address the problems introduced using the conventional plating compositions (i.e., compositions having a low concentration of copper and a high  
25 concentration of acid or visa versa) have not been completely satisfactory. For example, various additives have been used, such as particular suppressors, accelerators, and/or levelers in various concentrations. Other additives used include halide ions, such as chloride. The additives used depend upon whether the plating composition is a low

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copper concentration with a high acid concentration or the opposite, as is known to those persons of ordinary skill in the art. Certain additives may decrease the deposition rate of metal atoms at a given potential, thereby inhibiting the deposition process, whereas other additives may increase the deposition rate of metal ions at a given  
5 potential, thereby accelerating the deposition rate. Unfortunately, the available plating compositions have not sufficiently resolved the feature filling problems when dealing with the relatively high aspect ratio features in which the transport of metal ions is somewhat limited.

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### Summary

The electroplating compositions and electroplating methods of this invention, as described in detail hereinafter, provide surprisingly superior fill capabilities and ensure superior copper deposition with bottom-up fill capabilities for high aspect ratio features of submicron size such that the presence of voids is reduced or substantially eliminated  
15 altogether.

The electroplating compositions and methods may be utilized to electroplate a metal into device features, such as high aspect ratio semiconductor device trenches and/or contact holes on a semiconductor workpiece. The disclosed compositions and methods are applicable to a wide range of steps used in the manufacture of a  
20 metallization layer in a workpiece. For ease of explanation, the compositions and methods are discussed primarily in relation to metallization of features formed in a semiconductor wafer processed to form integrated circuits or other microelectronic components. The compositions and methods disclosed are not limited to such semiconductor wafers and features but may be used in connection with any  
25 semiconductor workpiece wherein metallization is required. The term "workpiece" is not limited to semiconductor wafers, but rather refers to substrates having generally parallel planar first and second surfaces and that are relatively thin, including semiconductor wafers, ceramic wafers, and other substrates upon which microelectronic

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circuits or components, data storage elements or layers, and/or micromechanical elements are formed.

The electroplating compositions include copper and acid at previously avoided relative concentrations. The electroplating compositions provide surprisingly superior  
5 fill capabilities, particularly copper deposition bottom-up fill capabilities for high aspect ratio features having submicron dimensions (e.g., 0.12  $\mu\text{m}$  trenches) such that the presence of voids is reduced or substantially eliminated altogether. Additionally, the electroplating compositions are less corrosive toward seed layers, also providing superior fill capabilities.

10 The electroplating compositions may comprise an aqueous mixture of copper and sulfuric acid wherein the ratio of copper concentration to sulfuric acid concentration (concentrations in g/L) is equal to from about 0.3 to about 0.8. They may also comprise an aqueous mixture of copper and sulfuric acid wherein the copper concentration is near its solubility limit when the sulfuric acid concentration is from about 65 to about  
15 150 g/L. These compositions may also include conventional additives, such as accelerators, suppressors, halides and/or levelers.

The disclosed methods utilize the electroplating compositions for depositing copper onto semiconductor workpieces. The methods further ensure superior copper deposition with bottom-up fill capabilities for high aspect ratio features of submicron  
20 size such that the presence of voids is reduced or substantially eliminated altogether.

### **Brief Description of the Drawings**

Fig. 1 is a graph illustrating the solubility of copper sulfate in sulfuric acid at about 25°C.

25 Figs. 2(a)-2(e) are scanning electron microscope (SEM) photographs of copper semiconductor interconnects measuring from about 0.12  $\mu\text{m}$  to about 0.15  $\mu\text{m}$  in width at half the height of the interconnect formed by using various embodiments of the

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electroplating compositions wherein the copper concentration was varied while the acid concentration was about 80 g/L.

Fig. 2(f) is a pictured leverage plot showing feature fill results when comparing varied acid/copper electroplating compositions, where the copper concentration was increased in successive samples.

Figs. 3(a)-3(d) are SEM photographs of copper semiconductor interconnects measuring about 0.15  $\mu\text{m}$  in width at half the height of the interconnect formed using various embodiments of the electroplating compositions wherein the acid concentration was varied while the copper concentration was about 20 g/L (in Figs. 3(a)-(b)) and about 50 g/L (in Figs. 3(c)-(d)).

Fig. 3(e) is an SEM photograph of an interconnect trench measuring about 0.023  $\mu\text{m}$  in width at half the height of the interconnect trench prior to electroplating.

Fig. 3(f) is a pictured leverage plot showing the feature fill results when comparing varied acid/copper electroplating compositions, wherein the acid concentration was increased in successive samples.

Figs. 4(a)-4(c) are SEM photographs of copper semiconductor interconnects measuring about 0.25  $\mu\text{m}$  in width at half the interconnect height formed using a prior art electroplating composition wherein the copper concentration was about 50 g/L while the acid concentration was about 10 g/L.

Figs. 4(d)-4(f) are SEM photographs of copper semiconductor interconnects measuring about 0.25  $\mu\text{m}$  in width at half the interconnect height formed using an embodiment of the electroplating compositions of this invention wherein the copper concentration was about 50 g/L while the acid concentration was about 80g/L.

Fig. 5(a) is an SEM photograph of copper semiconductor interconnects measuring about 0.2  $\mu\text{m}$  in width at half the height of the interconnect formed using a prior art electroplating composition wherein the copper concentration was about 20 g/L while the acid concentration was about 180 g/L

Fig. 5(b) is an SEM photo of copper semiconductor interconnects measuring

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about 0.2  $\mu\text{m}$  in width at half the height of the interconnect formed using an embodiment of the electroplating compositions of this invention wherein the copper concentration was about 50 g/L while the acid concentration was about 80g/L.

Fig. 6(a) is an SEM photograph of a copper semiconductor via measuring about  
5 0.16  $\mu\text{m}$  in width at half the height of the via formed using a prior art electroplating composition wherein the copper concentration was about 20 g/L while the acid concentration was about 180 g/L.

Fig. 6(b) is an SEM photograph of a copper semiconductor via measuring about  
10 0.16  $\mu\text{m}$  in width at half the height of the via formed using an embodiment of the electroplating compositions of this embodiment of this invention wherein the copper concentration was about 40 g/L while the acid concentration was about 100 g/L.

Fig. 7(a) is a cross-sectional view of a representative electroprocessing station having a processing chamber or reactor for use in a processing tool with which the electrochemical compositions may be utilized.

15 Fig. 7(b) is a cross-sectional view of a portion of a representative processing chamber or reactor with which the electrochemical compositions may be utilized.

Figs. 8(a)-8(d) are representative process flow charts illustrating a few of many possible manners of implementing metallization of a semiconductor workpiece utilizing the electrochemical compositions and methods of this invention.

20 Figs. 9(a) and 9(b) illustrate two representative processing tools with which the electroplating compositions may be utilized.

### **Detailed Description**

25 Conventional electroplating compositions of copper and acid, such as sulfuric acid, comprise either a relatively low acid concentration whenever there is a relatively high copper concentration to reduce the terminal effect and provide reasonable filling capability, or a relatively high acid concentration whenever there is a relatively low copper concentration so that the plating composition will have good throwing power.



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The electroplating compositions of this invention do not follow such conventional wisdom. Instead, they include copper concentrations more equivalent to the acid concentrations.

In particular embodiments the electroplating compositions formulated in accordance with this invention comprise an aqueous mixture of copper and sulfuric acid wherein the ratio of the copper concentration to the sulfuric acid concentration (all concentrations listed in g/L are grams per liter of solution) is equal to from about 0.3 to about 0.8 g/L. In other particular embodiments the electroplating compositions comprise a mixture of copper and sulfuric acid wherein the ratio of the copper concentration to the sulfuric acid concentration is equal to from about 0.4 to about 0.7 g/L. In yet other embodiments the electroplating compositions comprise a mixture of copper and sulfuric acid wherein the ratio of the copper concentration to the sulfuric acid concentration is equal to from about 0.5 to about 0.6 g/L.

In other embodiments the electroplating compositions comprise an aqueous mixture of copper and sulfuric acid wherein the copper concentration in the composition is within about 60% to about 90% of its solubility limit when the sulfuric acid concentration is from about 65 to about 150 g/L. In yet other embodiments the electroplating compositions comprise an aqueous mixture of copper and sulfuric acid wherein the copper concentration in the composition is within about 60 % to about 90 % of its solubility limit when the sulfuric acid concentration is from about 70 to about 120 g/L. In other particular embodiments the compositions comprise an aqueous mixture of copper at a concentration of from about 35 to about 60 g/L and sulfuric acid at a concentration of from about 65 to about 150 g/L. In other embodiments the compositions comprise an aqueous mixture of copper at a concentration of from about 45 to about 55 g/L and sulfuric acid at a concentration of from about 75 to about 120 g/L.

Although any electroplating composition having acid and copper within the above disclosed ranges will provide superior fill capabilities, particularly useful

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electroplating compositions comprise an aqueous mixture of about 40 g/L copper and about 100 g/L sulfuric acid or about 50 g/L copper and about 80 g/L sulfuric acid. Other exemplary embodiments comprise aqueous mixtures of about 60 g/L copper and about 65 g/L sulfuric acid or about 47 g/L copper and about 70 g/L sulfuric acid.

5           The copper source used in the electroplating compositions of this invention may be, for example, a copper salt such as copper sulfate, copper fluoborate, copper gluconate, copper sulfamate, copper sulfonate, copper pyrophosphate, copper chloride, copper cyanide, combinations thereof, and the like. Although copper sulfate is primarily mentioned herein, it is to be understood that copper from any suitable source  
10       may be used in the disclosed compositions.

          The electroplating compositions may contain other mineral acids in combination with or in place of sulfuric acid, such as fluoboric acid and the like, organic acids, such as methane sulfonic (MSA), amidosulfuric, aminoacetic, and combinations thereof, and the like, combinations of mineral acids and organic acids. The electroplating  
15       compositions may include further additives such as suppressors, accelerators, and levelers to assist in filling small features.

          The electroplating compositions may also contain additives such as halide ions, for example chloride, bromide, iodide, combinations thereof, and the like. In certain embodiments of the disclosed compositions chloride is added in combination with  
20       certain suppressing additives (e.g., polyethers) in an amount sufficient to interact and suppress deposition of copper at constant voltage, or to increase the over potential for a given applied current density. As is known to those persons of ordinary skill in the art, the concentrations of halides added are typically determined by the operating parameters chosen for the particular hardware. In certain embodiments of the disclosed  
25       compositions the halogen concentration is from about 10 ppm to about 100 ppm. For example, about 50 ppm HCl may be added to an electroplating composition comprising about 50 g/L copper and about 80 g/L sulfuric acid. In another embodiment, about 20 ppm HCl is added to an electroplating composition comprising about 40 g/L copper and

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about 100 g/L sulfuric acid. Other suitable additives (as known to those persons of ordinary skill in the art) used to aid the suppressor in decreasing the deposition rate and/or to aid the accelerator in increasing the deposition rate may be added.

Suppressors generally increase cathodic polarization and adsorb on the substrate surface to inhibit or reduce copper deposition in the adsorbed areas. Suppressors added to the plating composition may include, e.g., two-element polyethylene glycol based suppressors, such as suppressors made of random/block copolymers of ethylene oxide and propylene oxide mixed in a wide range of ratios. For example, CUBATH ViaForm Suppressor (DF75), available from Enthone, Inc. of West Haven, CT, or Shipley C-3100 suppressor, available from Shipley Company of Marlborough, MA, may be used.

Embodiments of the electroplating compositions may include any suitable suppressor type and concentration. For example, CUBATH ViaForm DF75 suppressor at a concentration of from about 2 ml/L to about 30 ml/L, or about 2 to about 10 may be used. As further example, Shipley C-3100 suppressor at a concentration of from about 5 ml/L to about 25 ml/L, or about 10 to about 20 may be used. In one particular embodiment, about 2 ml/L of the CUBATH suppressor is used in an electroplating composition comprising about 50 g/L copper and about 80 g/L sulfuric acid. In another example, about 17.5 ml/L of Shipley C-3100 suppressor, available from Shipley Company of Marlborough, MA, is used in an electroplating composition comprising about 40 g/L copper and about 100 g/L sulfuric acid.

Accelerators reduce cathodic polarization and compete with suppressors for adsorption sites to accelerate copper growth in the adsorbed areas. The accelerators used in the plating composition may include, e.g., sulphur containing compounds, such as bis(sodium sulfopropyl)disulfide (SPS). Accelerators, with smaller molecular dimensions can diffuse faster than suppressors. For example, CUBATH ViaForm Accelerator (DF74) available from Enthone or Shipley B-3100 accelerator (available from Shipley), may be used. Embodiments of the electroplating compositions may include, for example, an accelerator such as the CUBATH ViaForm DF74. Such an

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accelerator may be used in any suitable concentration of from about 2 ml/L to about 30 ml/L, from about 2 to about 8 ml/L. For example, about 5 ml/L may be used in an electroplating composition comprising about 50 g/L copper and about 80 g/L sulfuric acid. For seed layers with superior coverage such as CVD, about 8 ml/L of this  
5 accelerator may be used. For seed layers with poor bottom coverage (e.g., bottom voids), about 2 ml/L of the DF74 or a like accelerator may be used. In another embodiment, about 10 ml/L of Shipley B-3100 accelerator (available from Shipley) is used in an electroplating composition comprising about 40 g/L copper and about 100 g/L sulfuric acid.

10 Suppressors and accelerators heavily populate around the features and since the suppressors inhibit the copper growth, a small overhang of the seed layer can close the mouth of the feature leading to a void in the feature. Therefore, an electroplating composition where the suppression is mostly active on the top of the topographical features and the accelerators dominate the suppressors in activity inside features so as to  
15 achieve bottom up growth may be particularly useful.

The concentrations of such components may vary to be optimized for particular hardware and/or operating conditions as desired. Suitable concentration ranges for additives (e.g., halides, accelerators, suppressors, optional levelers) to the electroplating compositions may vary depending upon the specific operating conditions for a  
20 particular chosen process and/or tool (e.g., temperature, spin speed, flow rate, current density) as is known to those persons of ordinary skill in the art.

Continued acceleration after filling the features may result in excess growth of copper over the features creating surface protrusions. Thus, the addition of a leveler, such as CUBATH ViaForm Leveler DF79, available from Enthone, or Shipley U-3100  
25 leveler (available from Shipley) may be added to the electroplating compositions disclosed herein. Other suitable levelers may be used to suppress the current at the protrusions to provide a leveled surface. Specific embodiments of the electroplating compositions include a leveler concentration of from about 0.5 ml/L to about 3 ml/L, or

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from about 1.0 to about 3.0 ml/L. For example, about 2.5 ml/L of the DF79 leveler may be used in an electroplating composition comprising about 50 g/L copper and about 80 g/L sulfuric acid. In another example, about 2 ml/L of Shipley U-3100 leveler (available from Shipley) may be used in an electroplating composition comprising  
5 about 40 g/L copper and about 100 g/L sulfuric acid.

The operating temperatures of electroplating compositions of this invention may range from about 15°C to about 30°C or from about 22°C to about 27°C. For example, an operating temperature of an electroplating composition comprising about 50 g/L copper and about 80 g/L sulfuric acid of about 25°C has been found useful.

10 The plating methods using electroplating compositions of this invention may be carried out, for example, in a fountain style plating reactor of the type currently marketed by Semitool, Inc. of Kalispell, MT, Novellus Systems, Inc., of San Jose, CA, or Applied Materials, Inc. of Santa Clara, CA. These tools typically incorporate plating reactors having an anode system that functions as a single anode, either by employing a  
15 single disc-like anode or a basket of anode particles.

However, the plating methods carried out in a multiple anode reactor of the type described in U.S. Patent Nos. 6,497,801, 6,569,297, 6,565,729 and in published PCT Application WO 00/61498 are particularly suited to using the electroplating compositions described herein. U.S. Patent Nos. 6,497,801, 6,569, 297, 6,565,729, and  
20 PCT Application WO 00/61498 are herein incorporated by reference.

Figure 7(a) illustrates a partial schematic, cross-sectional view of a representative plating station 110. A support member 140 includes a spin motor 144 and a rotor 142 coupled to the spin motor 144. The rotor 142 supports a contact assembly 160. The rotor 142 may include a backing plate 145 and a seal 141. The  
25 backing plate 145 moves transverse to a workpiece 101 (arrow T) between a first position (shown in solid lines in Figure 7(a)) in which the backing plate 145 contacts a backside of the workpiece 101 and a second position (shown in broken lines in Figure 7(a)) in which it is spaced apart from the backside of the workpiece 101.

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The contact assembly 160 may include a carrier 162, a plurality of contacts 164 carried by the carrier 162, and a plurality of shafts 166 extending between the carrier 162 and the rotor 142. The contacts 164 can be ring-type spring contacts or other types of contacts that are configured to engage a portion of the seed-layer on the workpiece

5 101. Commercially available support members 140 and contact assemblies 160 can be used. Particular suitable support members 140 and contact assemblies 160 are disclosed in U.S. Patent Nos. 6,228,232 and 6,080,691 and in U.S. Application Nos. 09/385,784; 09/386,803; 09/386,610; 09/386,197; 09/501,002; 09/733,608; and 09/804,696, all of which are herein incorporated by reference.

10 The plating station 110 may include a reactor vessel 130 having an outer housing or chamber 131 and an inner chamber 132 (both shown schematically in Figure 7(a)) disposed within the outer chamber 131. The inner chamber 132 carries at least one electrode (not shown in Figure 7(a)) and directs a flow of processing liquid, such as an embodiment of the electroplating compositions of this invention, to the workpiece

15 101. The processing liquid flows over a weir (as indicated by arrow F) and into the outer chamber 131, which captures the processing liquid for recirculation, recycling or disposal.

In operation, the support member 140 holds the workpiece 101 at a workpiece-processing site (such as a workpiece plane) of the reactor vessel 130 so that at least a

20 plating surface of the workpiece 101 engages the processing liquid. An electrical field is established in the processing liquid by applying an electrical potential between the plating surface of the workpiece 101 and one or more electrodes (described in greater detail below with reference to Figure 7(b)) positioned in the inner vessel 132. For example, in one process the contact assembly 160 is biased with a negative potential

25 with respect to the electrode(s) in the inner chamber 132 to plate conductive materials onto the workpiece 101. In one aspect of this process, one of the electrodes (a “thieving” electrode) is also biased with a negative potential with respect to the other

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electrodes to control the uniformity with which materials are applied to the workpiece 101.

Figure 7(b) is a schematic illustration of an embodiment of the reactor vessel 130 having multiple electrodes, including a thieving electrode. The reactor vessel 130 includes a helical drain channel 134 between the inner chamber 132 and the outer chamber 131. The drain channel 134 receives processing liquid, such as an embodiment of the electroplating compositions of this invention, overflowing the inner chamber 132 and guides the processing liquid toward a liquid outlet 135. Liquid enters the inner chamber 132 through a primary inlet 136a and a secondary inlet 136b. The primary inlet 136a is coupled to a primary flow channel 137 that directs a portion of the processing liquid within the inner chamber 132 to a primary flow guide 170. The primary flow guide 170 includes apertures 171 that direct the flow toward a central axis 139 of the inner chamber 132. The flow then proceeds upwardly from the primary flow guide 170 toward the workpiece feature to be filled.

The secondary inlet 136b may be coupled to a distributor 189 that directs a secondary liquid, for example the same or a different embodiment of the electroplating compositions of this invention, to a plurality of electrodes. The inner chamber 132 includes four concentric electrodes 180. A controller 183 is operatively coupled to the electrodes 180a-d to individually control the current applied to each electrode, and accordingly control the corresponding conductive paths between the electrodes and the workpiece feature.

The electrodes 180 are housed in a field shaping unit 176 having a corresponding plurality of electrode compartments 177 (shown as compartments 177a-177d) separated by partitions 178. The distributor 189 directs the secondary liquid into each compartment 177 via a corresponding plurality of distributor channels 179 (shown as distributor channels 179a-179d). Accordingly, the secondary liquid proceeds through the distributor 189, past the electrodes 180, and upwardly toward the workpiece feature. The effect of the field shaping unit 176 on the electrical field produced by the electrodes

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180 is as if the electrodes 180 were positioned at the exits of each compartment 177, as shown by virtual electrode positions 181a-181d.

The primary flow guide 170 forms an inwardly facing vessel wall 138 (indicated in dashed lines in Figure 7(b)) that extends upwardly and outwardly from the primary  
5 fluid inlet 136a. A shield 184 having an aperture 182 can be positioned between the electrodes 180 and the workpiece 101 feature to control the interaction between the workpiece feature and the fluid flow and electrical field within the reactor vessel 130.

In the reactor vessel 130 shown in Figure 7(b), each compartment 177 has one or more apertures 174 (e.g., holes and/or slots) through which liquid and gas bubbles  
10 pass. Accordingly, gas bubbles trapped in each compartment 177 proceed radially outwardly through the apertures 177 of each compartment until they exit the inner chamber 132. Each compartment 177 may include an interface member 175. The interface members 175 may include a filter or other element configured to trap air bubbles and other particulates, while allowing the secondary liquid to pass toward the  
15 workpiece feature. In another embodiment, the interface members 175 include ion membranes that allow ions to pass toward the workpiece feature, while preventing or substantially preventing the secondary fluid from passing toward the feature. Instead, the secondary fluid passes through the apertures 174 and out of the inner chamber 132 via the helical drain channel 134. The first fluid can be collected at a separate drain (not  
20 shown). In another embodiment, the ion membrane allows the fluid as well as ions to pass through.

One or more of the foregoing reactor assemblies may be readily integrated in a processing tool that is capable of executing a plurality of methods on a workpiece, such as a semiconductor microelectronic workpiece. One such processing tool is an  
25 electroplating apparatus available from Semitool, Inc. of Kalispell, MT. Figs. 9(a) and 9(b) illustrate such integration.

The system of Fig. 9(a) includes a plurality of processing stations 210. These processing stations include one or more rinsing/drying stations and one or more



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electroplating stations. (Other suitable immersion-chemical processing tools may be used with the electroplating compositions.) The system includes thermal processing stations, such as at 215, which include at least one thermal reactor that is adapted for rapid thermal processing (RTP).

5           The workpieces are transferred between processing stations 210 and the RTP station 215 using one or more robotic transfer mechanisms 220 that are disposed for linear movement along a central track 225. One or more of the stations 210 may also incorporate structures that are adapted for executing an in-situ rinse. All of the processing stations as well as the robotic transfer mechanisms may be disposed in a  
10 cabinet provided with filtered air at a positive pressure to thereby limit airborne contaminants that may reduce the effectiveness of the microelectronic workpiece processing.

Fig. 9(b) illustrates another representative processing tool in which the electroplating compositions of this invention may be used. The processing tool shown  
15 in Fig. 9(b) includes an RTP station 235 located in portion 230 that includes at least one thermal reactor, may be integrated into a tool set. Unlike the processing tool of Fig. 9(a), at least one thermal reactor is serviced by a dedicated robotic mechanism 240. The dedicated robotic mechanism 240 accepts workpieces that are transferred to it by the robotic transfer mechanisms 220. Transfer may take place through an intermediate  
20 staging door/area 245. As such, it becomes possible to hygienically separate the reactor portion 230 of the processing tool from other portions of the tool. Additionally, using such a construction, an annealing station may be implemented as a separate module that is attached to upgrade an existing tool set.

The electroplating compositions of this invention may be utilized with any of a  
25 myriad of workpiece metallization processing methods for forming interconnects and vias in a workpiece. For example, Figs. 8(a)-8(d) illustrate several possible electrochemical deposition metallization process flows wherein the disclosed

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electroplating compositions may be used to form interconnects, vias or other such features.

A typical Damascene process flow is illustrated in Fig. 8(a). In the Damascene process, the workpiece is first provided with a metallic seed layer and a barrier/adhesion layer that are disposed over a dielectric layer into which trenches (or other device features) are formed. The seed layer is used to conduct electrical current during a subsequent metal electroplating step. Typically the seed layer is a very thin layer of metal that can be applied using one of several methods. For example, the seed layer of metal can be laid down using physical vapor deposition or chemical vapor deposition methods to produce a layer on the order of about 500 Å thick. The seed layer can also be formed of copper, gold, nickel, palladium, and most or all other metals. The seed layer is formed over a surface that is convoluted by the presence of the trenches, or other device features, which are recessed into the dielectric substrate.

In certain methods, before using the electroplating compositions of this invention, an electrochemical (electroless or electrolytic) seed layer repair or enhancement step is performed (not shown in Fig. 8(a)). Specifically, a seed layer, such as an ultra-thin seed layer, may be repaired if needed to render the seed layer suitable for a subsequent metal deposition, or enhanced by depositing additional metal on the existing seed layer, in a separate deposition step to provide an "enhanced" seed layer. The enhanced seed layer typically has a thickness at all points on sidewalls of substantially all recessed features distributed within the workpiece that is equal to or greater than about 10% of the nominal seed layer thickness over an exteriorly disposed surface of the workpiece. For example a seed layer enhancement process may be performed as disclosed in U.S. Patent Nos. 6,290,833 and 6,565, 729, which are incorporated herein by reference. When a seed layer enhancement process is performed, it may be followed by a rinsing step.

With continued reference to Fig. 8(a), a copper layer is electroplated onto the seed layer in the form of a blanket layer. The blanket layer is plated to an extent which

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forms an overlying layer, to provide a copper layer that fills the trenches (or other device features) used to form the interconnect wiring. The copper layer may optionally then be rinsed, typically in DI water and (optionally) dried. The rinsing/drying, if performed, may occur in the chamber in which the electrochemical plating occurs or in  
5 separate chambers depending upon the plating tool used.

Subsequently, excess copper is removed by transferring the workpiece to a stripping unit to, e.g., bevel-etch the excess copper. In certain methods using the electroplating compositions disclosed herein, excess copper is selectively removed from, for example, a backside of the workpiece and/or a peripheral edge of a process  
10 side of a workpiece, using methods such as those disclosed in U.S. Patent No. 6,413,436, which is incorporated herein by reference. The bevel etched and back side cleaned workpiece may then be rinsed. The backside clean and initial DI rinse can occur simultaneously.

Each of the plating, rinsing and etching steps can be performed in the same  
15 chamber or can be performed in separate chambers. The etched workpiece is subsequently annealed. The workpiece may be rinsed with, e.g., DI water, prior to annealing. The workpiece may be annealed using any suitable method. For example, the workpiece may be annealed using conventional furnace methods or may be annealed at temperatures below 100°C, or even at ambient room temperature, using methods such  
20 as those disclosed in U.S. Patent No. 6,508,920, which patent is incorporated herein by reference. The workpiece may then be chemically mechanically polished to, for example, remove copper that is deposited in excess of what is desired for the device features.

As shown in Fig. 8(b), an alternative process utilizing the electroplating  
25 compositions of this invention may include a preclean or pre-wet step prior to copper plating so as to limit surface defects and remove waste materials therefrom. As shown in Fig. 8(b), the preclean or pre-wet step, copper plating, backside clean and/ or bevel

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etch and DI rinsing steps may all take place in the plating tool. The anneal and CMP steps may then follow outside the plating tool.

In another possible process suitable for use of the electroplating compositions of this invention, a seed layer repair or enhancement step may be performed prior to  
5 copper plating (Fig. 8c)). The seed layer repair step may comprise electrochemically depositing a second seed layer followed by a DI rinse. The second seed layer deposition may be performed by any suitable means, such as discussed above. As shown in Fig. 8(c), the seed repair, copper plating, backside clean and/or bevel etch and DI rinsing steps may all take place in the plating tool. The anneal and CMP steps may  
10 then follow outside the plating tool.

As shown in Fig. 8(d), in another alternative process utilizing the electroplating compositions of this invention, the copper plating, back side clean/bevel etch, DI rinsing and anneal steps may all take place in the plating tool. CMP may then be performed outside the plating tool.

15 As discussed above, the electroplating compositions of this invention may be used in a number of electroplating tools using any of a variety of workpiece metallization processing methods. In addition, a number of process parameters may be used for the metallization process using the electroplating compositions disclosed herein. The process parameters utilized depend upon the features to be filled, the tool  
20 being used and other such variables as know to those persons skilled in the art. One possible process is set forth below as a representative example only.

During the electrochemical deposition of copper into device features, such as interconnects and/or vias on a workpiece (according to one of the methods discussed above or any other suitable method) acidic electroplating compositions can corrode  
25 (etch) thin seed layers leading to the formation of voids. Accordingly, a workpiece loading bias, for example, from about 0.1 V to about 1.0 V may be applied to the workpiece plating surface while the workpiece is being immersed in an embodiment of the disclosed electroplating composition. For example, a loading bias of about 0.4 V or

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greater for 200 mm workpieces have been found to provide a void free fill of the features. To further enhance plating, for example, for plating a 1.0  $\mu\text{m}$  copper deposition on a 200 mm wafer, the wafer may be rotated upon immersion into the electroplating composition between about 40 rpm and about 200 rpm. Upon plating, the  
5 wafer is rotated between about 10 rpm and about 150 rpm. Exemplary embodiments of the plating methods rotate the wafer upon immersion at about 75 rpm and upon plating at about, 75 rpm at 1.0 amp for 5 seconds, 40 rpm at 1.0 amp for 25 seconds, and 40 rpm at 4.5 amps for the remaining time necessary to deposit the desired thickness. As is known to persons skilled in the art, the rotation speeds, biases, and time periods utilized  
10 depend upon the plating tool used and the device to be formed.

To further enhance plating, for example, for plating a 0.85  $\mu\text{m}$  copper deposition on a 200 mm wafer, the wafer was rotated upon immersion into the plating composition at between about 40 rpm and about 200 rpm. Upon plating the wafer is rotated between about 10 rpm and about 150 rpm. Exemplary embodiments of the plating methods  
15 rotate the wafer upon immersion at about 75 rpm and upon plating at about, 75 rpm at 1.0 amp for 5 seconds, 40 rpm at 1.0 amp for 5 seconds, 40 rpm at 2.0 amp for 39 seconds, and 60 rpm at 8.22 amp until the desired thickness is achieved.

Alternatively, and using current density designations for further description of possible plating enhancing methods, a 1  $\mu\text{m}$  copper deposition may be deposited on  
20 200 mm wafer having a copper seed layer of about 400 Å. The wafer may be rotated at about 150 rpm. The current density may be from about 2 mAmps/cm<sup>2</sup> to about 70 mAmps/cm<sup>2</sup>. Alternatively, the current density may be from about 3 mAmps/cm<sup>2</sup> to about 25 mAmps/cm<sup>2</sup> for a time period in which the desired thickness is achieved. Of course, the current density utilized can be varied during the plating process, typically  
25 but not exclusively starting at a low current density and finishing with a higher current density.

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**Example 1 and Comparative Data**

A representative embodiment of the electroplating composition of this invention is shown in Table 1.

**Table 1**

5	<u>Component</u>	<u>Concentration g/L</u>
	Cu	50
	H <sub>2</sub> SO <sub>4</sub>	80
	Accelerator (DF74)	5.0
	Suppressor (DF75)	2.0
10	Leveler (DF79)	2.5
	HCL	50*

\* Halogen concentration in ppm.

With suitable current densities (such as those set forth above), void free filling  
15 was achieved with this embodiment of the electrochemical composition, as illustrated in the results shown in Figs. 2(e), 3(d), 4(d)-4(f) and 5(b).

For comparison purposes, prior art electroplating compositions were tested under the same conditions with identical additives at the identical concentrations. Features having voids, as can be seen in Figs. 4(a) – 4(c) were obtained. Specifically,  
20 prior art electroplating compositions comprising the conventional high copper and low acid combination (i.e., 50 g/L Cu and 10 g/L sulfuric acid) produced vias having visible voids. A comparison of the results shown in Figs. 4(a)-(c) versus 4(d)-(f) reveal that the prior art high copper/low acid electroplating compositions (Figs. 4(a)-(c)) result in the formation of interconnects having significant voids, seen as dark spots in the  
25 micrographs at the lower regions of the interconnects. Although the filling of the interconnects using one embodiment of the electroplating compositions of this invention as shown in Fig. 4(d) was halted prior to completely filling the interconnect trench, as can be seen in the micrograph of 4(d), the interconnects were forming without visible

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voids – a significant improvement over the conventional electroplating composition results. Additionally, although the interconnects formed using an embodiment of the electroplating compositions as shown in Fig. 4(f) show some voiding, the number and size of the voids in the interconnects are significantly fewer and smaller as compared to the resulting voiding in interconnects formed using the prior art high copper/low acid electroplating composition, as can be seen in the microphotograph of Fig. 4(c).

For further comparison, another prior art electroplating composition (i.e., a conventional low copper/high acid composition) was tested under the same conditions with identical additives (at identical concentrations) resulting in trenches having seam voids as is illustrated in Fig. 5(a). Specifically, a prior art electroplating composition comprising 20 g/L Cu and 180 g/L sulfuric acid produced seam voids in metallized trenches. In comparison, an embodiment of the electrochemical plating compositions of this invention, specifically a composition comprising 80 g/L sulfuric acid and 50 g/L Cu, produced void free features in the identical size trenches (as shown in Fig. 5(b)).

#### **Example 2 and Comparative Data**

Another embodiment of the electroplating composition of this invention is shown in Table 2.

**Table 2**

<u>Component</u>	<u>Concentration g/L</u>
Cu	40
H <sub>2</sub> SO <sub>4</sub>	100
Accelerator (B-3100)	10.0
Suppressor (C-3100)	17.5
Leveler (U-3100)	3.0

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HCL

20\*

\* Halogen concentration in ppm.

5 With suitable current densities, such as those set forth above, void free filling of a via was achieved with this embodiment of the electroplating composition of this invention as is illustrated in Fig. 6(b).

For comparison purposes, a prior art electroplating composition was tested under the same conditions with identical additives (at identical concentrations) as was Example 2. A via fill having voids, as can be seen in Fig. 6(a), was obtained with the prior art composition. Specifically, the prior art electroplating composition compared had the conventional high acid and low copper combination (i.e., 20 g/L Cu and 180 g/L sulfuric acid) producing a via having visible voids, as shown in Fig. 6(a) while the embodiments of the electroplating compositions of this invention showed surprisingly superior results, a void-free via filling was achieved, as shown in Fig. 6(b).

15

### **Example 3**

As shown in Figs. 2(a) through 2(e), copper semiconductor interconnect trenches measuring about 0.12 to about 0.15  $\mu\text{m}$  in width at half the height of the interconnect were filled using various embodiments of the electroplating compositions wherein the copper concentration was varied while the acid concentration was about 80 g/L and were compared to various prior art compositions. Specifically, as shown in Figs. 2(a) and 2(c), interconnect trenches were filled utilizing a prior art electroplating composition comprising 20 g/L copper and 80 g/L acid. As can be seen in the micrographs of these figures, the prior art low copper/high acid compositions result in devices having visible voids. In comparison, however, as shown in Figs. 2(b) and (d), the electroplating compositions of this invention having copper and acid concentrations near the copper solubility limit resulted in devices having a relatively low number of voids formed. Specifically, as shown in Figs. 2(b) and 2(d), interconnect trenches were

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filled utilizing an electroplating composition comprising 35 g/L copper and 80 g/L acid providing superior results.

#### **Example 4**

5           As the Fig. 2(f) tabulated results show a number of example electroplating compositions tested wherein the copper concentration was increased step-wise and the acid concentrations were kept relatively low. This increase in copper concentration relative to the low acid concentration (contrary to conventional wisdom) again gave surprisingly superior results.

10           Specifically, the additive concentrations and halide concentrations were held constant while the acid and copper concentrations were varied from 10g/l to 150g/l and from 20g/l to 50g/l, respectively. After plating, the plated wafers were cross-sectioned and examined for the presence of voids. For each example of electroplating compositions tested, five filled features at each of three sizes (0.12, 0.15, 0.20  $\mu\text{ms}$ )  
15           were examined. The number of features filled out of five was tallied for each size. A perfect score would be 5 at each size. This data was then entered into a statistical analysis software tool (i.e., a JMP statistical analysis software program) that generated the pictured leverage plot shown in Fig. 2(f). As can be seen from Fig. 2(f), electroplating compositions wherein the copper concentration was relatively high and  
20           the acid concentration was relatively low (i.e., embodiments of the electroplating compositions of this invention wherein copper concentrations were near solubility limits) provide a statistically significant improvement in feature bottom-up fill capabilities

#### **Example 5 and Comparative Data**

25           As shown in Figs. 3(a)-3(d), copper semiconductor interconnect trenches measuring about 0.15  $\mu\text{m}$  in width at half the height of the interconnect were filled using electroplating compositions wherein the sulfuric acid concentration was varied

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while the copper concentration was 20 g/L or 50 g/L (20 g/L Cu and 80 and 150 g/L acid, respectively in Figs. 3(a)-(b)) and 50 g/L Cu with 10 and 80 g/L acid, respectively in Figs. 3(c)-(d)). As shown in Fig. 3(a), an interconnect trench was filled utilizing an electroplating composition comprising 20 g/L copper and 80 g/L acid.

5 For comparison purposes, as shown in Fig. 3(b), an interconnect trench was filled utilizing an electroplating composition comprising 20 g/L copper and 150 g/L sulfuric acid – like the typical conventional high acid/low copper compositions. Again, inferior results are achieved with such a composition.

For further comparison purposes, as shown in Fig. 3(c), an interconnect trench  
10 was filled utilizing an electrochemical composition comprising 50 g/L copper and 10 g/L sulfuric acid. Results are shown in Fig. 3(c). (The results shown in Fig. 3(d) show the superior results achieved with the electroplating composition of this invention as described above in Example 1.)

#### 15 **Example 6**

As the Fig. 3(f) tabulated results further demonstrate, increasing the acid concentration while increasing the copper concentration so that it is at or near its solubility limit provides a statistically significant improvement in feature fill. A number of example electroplating compositions were tested wherein the acid  
20 concentration was increased step-wise and the copper concentrations were kept relatively high – near its solubility limits for the particular acid concentrations.

Specifically, the additive concentrations and halide concentrations were held constant while the acid and copper concentrations were varied from 10g/l to 150g/l and from 20g/l to 50g/l, respectively. After plating, the plated wafers were cross-sectioned  
25 and examined for the presence of voids. For each example of electroplating composition tested, five filled features at each of three sizes (0.12, 0.15, 0.20  $\mu\text{ms}$ ) were examined. The number of features filled out of five was tallied for each size. A perfect score would be 5 at each size. This data was then entered into a statistical analysis

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software tool (i.e., a JMP statistical analysis software program) that generated the pictured leverage plot shown in Fig. 3(f). As can be seen from Fig. 3(f), electroplating compositions wherein the copper concentration was at or near its solubility limit provide statistically significant improvement in feature bottom-up fill capabilities.

5           Whereas the electroplating compositions and methods of this invention have been described with reference to multiple embodiments and examples, it will be understood that the invention is not limited to those embodiments and examples. On the contrary, the invention is intended to encompass all modifications, alternatives, and equivalents as may be included within the spirit and scope of the invention as defined  
10 by the appended claims.